

Supporting Information Available

Structure and Absolute Configuration of Helosides A and B, New Saponins from *Chamaelirium luteum*

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Table S1. ¹H (750 MHz) and ¹³C (188 MHz) NMR Spectroscopic Data for Heloside A (**1**) (δ in ppm, pyridine-*d*₅).

	Aglycone					Sugars		
	¹ H [δ, mult., <i>J</i> (Hz)]	¹³ C	HMBC (H → C)	ROESY		¹ H [δ, mult., <i>J</i> (Hz)]	¹³ C	HMBC (H → C)
1α	1.37 dt (3.6, 14.3)	39.7	C-10, C-19	H-2α, H-3, H-9	3- <i>O</i> -β-D-Glucose			
1β	3.21 td (3.4, 13.9)			H-2β, H-19	1'	5.07 d (7.8)	102.4	C-3
2α	2.15 m	30.5		H-1α, H-3	2'	4.06 t (8.0)	75.3 ^b	
2β	1.91 m ^a			H-1β, H-4β	3'	4.31 t (8.9)	78.6 ^c	
3	4.02 m ^a	78.3	C-1'	H-1α, H-2α, H-4α	4'	4.29 t (8.8)	71.7	
4α	2.78 ddd (2.1, 4.7, 13.1)	39.9	C-2, C-3, C-5, C-6, C-10	H-3	5'	3.97 m	78.5	
4β	2.58 m ^a			H-2β, H-19	6a'	4.40 dd (4.4, 11.8)	62.8 ^d	
5		141.8			6b'	4.53 br d (11.8)		
6	5.42 d (5.7)	121.7	C-4, C-7, C-8, C-10		26- <i>O</i> -β-D-Glucose			
7α	1.60 m	32.4		H-14	1''	4.81 d (7.8)	104.9	C-26
7β	1.93 m ^a			H-8	2''	4.02 t (8.1)	75.4 ^b	
8	1.53 m	31.8	C-7, C-14	H-7β, H-11, H-18, H-19	3''	4.24 t (8.9)	78.7 ^c	
9	1.28 m ^a	57.2	C-8, C-11, C-19	H-1α	4''	4.22 t (8.6)	71.8	
10		38.9			5''	3.93 m	78.5	
11	4.31 m ^a	68.2		H-12β, H-18, H-19	6a''	4.37 dd (5.7, 11.9)	62.9 ^d	
12α	1.58 m ^a	52.3	C-9, C-11, C-13, C-14, C-18	H-14	6b''	4.55 br d (11.9)		
12β	2.61 dd (4.7, 12.0)			H-11, H-18				
13		43.4						
14	1.08 ddd (7.4, 11.1, 13.2)	54.5	C-13, C-18	H-12α, H-15α, H-17				
15α	2.27 td (7.6, 12.7)	37.2	C-13, C-17	H-14, H-16				
15β	1.50 dt (4.5, 13.3)			H-18				
16	4.76 m	71.7		H-15α, H-17				
17	1.72 dd (6.9, 10.9)	58.1	C-13, C-16, C-18, C-20	H-16				
18	1.22 s	14.8	C-12, C-13, C-14, C-17	H-8, H-11, H-12β, H-15β, H-20				
19	1.28 s	19.1	C-1, C-5, C-9, C-10	H-1β, H-4β, H-8, H-11				
20	2.54 m ^a	36.1	C-17, C-21, C-22	H-18, H-21				
21	1.18 d (7.0)	15.0	C-17, C-20, C-22					
22	4.15 m	75.1						
23a, b	1.74 m ^a	31.8	C-22					
24a	1.30 m ^a	31.6	C-25, C-27					
24b	2.07 m							
25	1.96 octet (6.7)	34.3	C-24, C-26, C-27					
26a	3.62 dd (5.9, 9.5)	75.3	C-24, C-25, C-27, C-1''					
26b	3.92 dd (7.0, 9.5)							
27	0.99 d (6.7)	17.7	C-24, C-25, C-26					

^a Indicates overlapping signals.^{b, c, d} Assignments are interchangeable within column.

Table S2. ¹H (750 MHz) and ¹³C (188 MHz) NMR Spectroscopic Data for Heloside B (**2**) (δ in ppm, pyridine-*d*₅).

	Aglycone					Sugars		
	¹ H [δ, mult., <i>J</i> (Hz)]	¹³ C	HMBC (H → C)	ROESY		¹ H [δ, mult., <i>J</i> (Hz)]	¹³ C	HMBC (H → C)
1α	1.37 m ^a	39.7	C-2, C-10, C-19	H-2α, H-3	3- <i>O</i> -β-D-Glucose			
1β	3.22 dt (3.2, 13.9)			H-19	1'	5.07 d (7.7)	102.4	C-3
2α	2.15 m	30.5		H-1α, H-3	2'	4.05 t (8.3)	75.4	
2β	1.91 m ^a			H-1β, H-19	3'	4.31 t (8.7)	78.7	
3	4.02 m	78.3	C-1'	H-1α, H-2α, H-4α	4'	4.29 t (8.7)	71.8 ^b	
4α	2.78 ddd (2.0, 4.6, 13.1)	39.9	C-2, C-3, C-5, C-10	H-3	5'	3.97 m	78.5	
4β	2.58 m ^a			H-2β, H-19	6a'	4.40 dd (5.4, 11.9)	62.8	
5		141.8			6b'	4.53 br d (11.9)		
6	5.43 d (5.5)	121.7	C-4, C-7, C-8, C-10					
7α	1.61 m	32.4		H-14				
7β	1.94 m ^a			H-8				
8	1.54 m ^a	31.8	C-9, C-14	H-7β, H-18				
9	1.29 m ^a	57.2	C-8, C-10, C-11, C-19	H-1α				
10		38.9						
11	4.31 m ^a	68.2	C-10	H-8, H-12β, H-18, H-19				
12α	1.58 m ^a	52.4	C-9, C-11, C-13, C-14	H-9, H-17				
12β	2.61 dd (4.8, 12.1)			H-11, H-18				
13		43.4						
14	1.08 m ^a	54.5	C-13, C-15, C-18	H-12α, H-15α				
15α	2.27 td (7.5, 12.7)	37.2	C-13, C-14, C-16, C-17	H-14, H-16				
15β	1.50 dt (4.4, 13.1)			H-18				
16	4.77 tt (3.8, 7.4)	71.7 ^b		H-15α, H-17				
17	1.73 dd (7.0, 11.1)	58.1	C-12, C-13, C-18, C-20	H-16				
18	1.23 s	14.8	C-12, C-13, C-14, C-17	H-11, H-15β, H-20				
19	1.28 s	19.1	C-1, C-5, C-10, C-19	H-1β, H-2β, H-4β, H-11				
20	2.60 m ^a	36.0		H-18				
21	1.19 d (7.1)	15.1	C-17, C-20, C-22					
22	4.21 m	75.4	C-21					
23a, b	1.84 m ^a	32.0	C-22, C-24					
24a	1.39 m	31.5	C-23, C-25, C-26, C-27					
24b	2.20 m							
25	1.91 m ^a	37.0	C-24, C-26, C-27					
26a	3.69 td (5.5, 10.7)	67.6	C-24, C-25, C-27					
26b	3.78 td (5.3, 10.5)							
27	1.09 d (6.7)	17.7	C-24, C-25, C-26					

^a Indicates overlapping signals.^b Assignments are interchangeable.





